[2]The frequency of the fully symmetrical valence vibration ν_1 ($\Sigma+$) of the ion HF_2^- lies near 600 cm^{-1} (Ref. 14). The frequencies of the remaining vibrations $\nu_2(\pi)$ and $\nu_3(\Sigma+)$ at T = 293°K are equal to 1257 and 1522 cm^{-1} in KBr (ω_m = 165 cm^{-1}) and 1258 and 1458 cm^{-1} in RbI (ω_m = 103 cm^{-1}, Ref. 15).

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Photoluminescence of alkali halide crystals excited by vacuum ultraviolet H_2 laser radiation

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An investigation was made of the luminescence of NaCl and KBr crystals under the action of vacuum ultraviolet ($\lambda = 1600$ Å) radiation emitted from an H_2 laser. The peak excitation intensity was approximately 10 orders of magnitude higher than that used previously. The spectra and time characteristics of the luminescence were obtained and compared with the case when the luminescence was excited by radiation of a hydrogen lamp emitting in the same spectral range. Conditions under which nonlinear effects should appear in alkali halide crystals were considered.

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1. The development of vacuum ultraviolet (VUV) lasers has made it possible to study the luminescence of wide-gap materials, such as alkali-halide crystals, at high photoexcitation intensities. One of the most promising systems is a VUV hydrogen laser,[1] which can emit short and sufficiently powerful pulses of radiation in the region of 1600 Å at a high repetition frequency. The interest in strong photoexcitation of alkali-halide crystals arises from the likelihood of observing nonlinear effects at high exciton concentrations and also from the possibility of constructing compact tunable ultraviolet lasers emitting in the range 2000 Å $\lesssim \lambda \lesssim$ 3000 Å.

We shall describe a study of the luminescence of NaCl and KBr crystals excited with a VUV H_2 laser (λ = 1600 Å) at a peak photoexcitation intensity approximately ten orders of magnitude higher than that used previously. We shall consider the conditions under which nonlinear effects should appear in alkali-halide crystals. Some preliminary results, obtained with a fast-response recording system, can be found in Ref. 2.

2. We used a modified hydrogen laser[3] with a total energy of 1.5–2 μJ per pulse, emitted in the form of 10 closely spaced lines in the region of 1610 Å. The duration of the laser pulses was less than 1 nsec and the pulse repetition frequency was up to 20 Hz. The divergence of the laser beam at the exit from a discharge channel (0.01 × 1 × 30 cm) was 2–3° in the channel plane and 0.1° at right angles to this plane. The laser pulse energy was measured with a thermopile calibrated with the aid of blackbody radiation. These energy measurements were accurate to within 50%. The laser radiation was directed onto a given sample through an N_2O cell characterized by a known transmission; this cell was used to attenuate the laser radiation in the region of 1600 Å and to remove the radiation in the region of 1200 Å (Fig. 1). The laser radiation was focused on the surface of a crystal by an LiF lens with a focal length of 60 mm and this was checked by examination of the visible luminescence under a microscope. The laser power density reaching an area of 0.8 × 0.4 mm was then 0.3 mW/cm^2.

Crystals with polished or cleaved surfaces were bonded to a heat sink of a helium cryostat at an angle of about 30° with respect to the laser beam. A junction of a calibrated thermocouple, bonded directly to the crystal

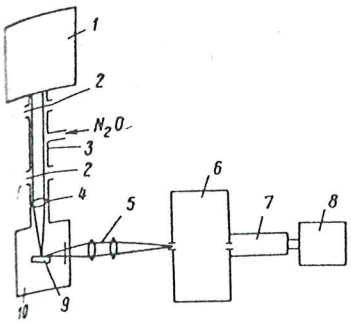


FIG. 1. Schematic diagram of the apparatus: 1) hydrogen laser; 2) LiF window; 3) cell with buffer gas; 4) LiF lens (f = 60 mm); 5) condenser system; 6) MDR-2 monochromator; 7) FÉU-39 photomultiplier; 8) S8-2 oscillograph; 9) investigated crystal; 10) cryostat.

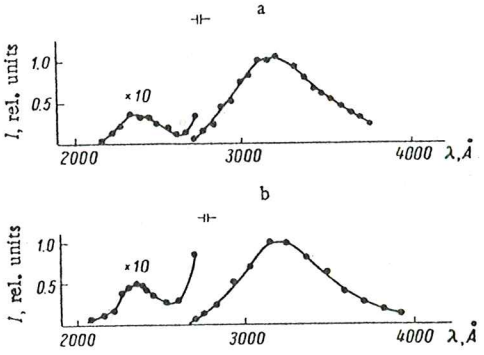


FIG. 2. Luminescence spectra of an NaCl crystal (T = 80°K) excited with: a) hydrogen laser radiation, λ = 1610 Å, $\Delta\lambda_{exc}$ = 8 Å; b) hydrogen lamp radiation, λ = 1610 Å, $\Delta\lambda_{exc}$ = 50 Å.

surface, was used to measure the temperature of the crystal. The illuminated part of the crystal was projected, by a condenser system with a relative aperture 1 : 2, onto the entry slit of an MDR-2 monochromator. The luminescence was recorded with an FÉU-39A photomultiplier and an oscillograph. The luminescence decay time was measured with a resolution of up to 40 nsec. The time constant of the measuring channel used in recording the spectra was 8 μsec.

For comparison, we recorded also the luminescence spectra under weak excitation conditions, in which case we employed a capillary hydrogen lamp (current 100 mA, voltage 1.5 kV), whose radiation was passed through a VMS-1 monochromator and then directed to the investigated sample. This lamp was placed next to the entry slit of the monochromator without any intermediate windows. The spectral width at the exit from the monochromator was varied within the range 10-50 Å. The luminescence signal at the photomultiplier output was recorded with a galvanometer. We used crystals without significant absorption bands in the $\lambda > 2000$ Å range.

3. Figure 2 shows the spectrum of the luminescence of an NaCl crystal excited with the hydrogen laser radiation (a) and, for comparison, with the hydrogen lamp radiation (b). The difference between the excitation intensities in these two cases was approximately ten orders of magnitude. The spectrum consisted of two bands, one at long wavelengths with a maximum at λ = 3190 Å (3.87 ± 0.04 eV) and the other at short wavelengths with a maximum at λ = 2350 Å (5.23 ± 0.03 eV); the decay times of these two bands were 40 nsec and 120 μsec, respectively. The positions of the luminescence bands obtained under laser excitation conditions were exactly the same as in the case of excitation with the hydrogen lamp radiation. The ratio of the intensities of the short-wavelength luminescence to the long-wavelength band was I(5.23 eV)/I(3.87 eV) = 0.051 in the laser excitation case and I(5.23 eV)/(3.87 eV) = 0.036 for the hydrogen lamp excitation.

We also determined the temperature dependences of the intensities of the 5.25 and 3.87 eV luminescence bands under laser excitation conditions (Fig. 3). When the temperature was increased to 140°K the intensities of both bands remained practically constant. Above 150°K the intensity began to fall rapidly. The fall was faster for the 3.87 eV band than for the 5.25 eV band.

The temperature dependences of the duration of the long-wavelength luminescence was similar.

The intensity of the short-wavelength luminescence was a linear function of the laser radiation energy when the latter was varied by two orders of magnitude.

The luminescence spectra differed from those reported in Ref. 4 for pure crystals. In fact, the short-wavelength luminescence peak emitted by pure crystals had a maximum at λ = 2320 Å (5.35 eV) and the long-wavelength peak was much weaker and occurred at λ = 3700 Å (3.35 eV). These differences could not be attributed to nonlinear effects because the luminescence spectra were basically similar under strong and weak excitation conditions. The observed difference between the spectra might be attributed to the presence of bromine impurities in our crystals. Even very small amounts of these impurities are known to affect considerably the luminescence of NaCl crystals.[5,6] The absorption line of isolated Br^- ions with a maximum at 7.72 eV is located in the long-wavelength wing of the first exciton absorption line of NaCl. This bromine line coincides with the hydrogen laser energy. Photons of this energy excite efficiently the luminescence whose spectrum consists of two lines with maxima at 5.15 and 3.9 eV. The long-wavelength band is due to the radiative decay of self-localized excitons of the $BrCl^- + e$ type and the short-wavelength band is due to the decay of self-localized electrons of the $Br_2^- + e$ type. The position of

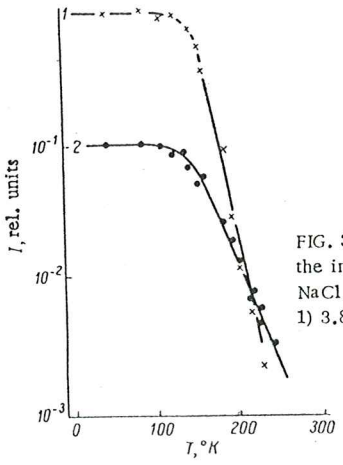


FIG. 3. Temperature dependences of the intensity of the luminescence of NaCl under laser excitation conditions: 1) 3.87 eV band; 2) 5.23 eV band.

the short-wavelength band is a function of the concentration of the bromine ions and it shifts toward higher energies when this concentration is reduced. The intensity ratio I(5.15 eV/I(3.9 eV) is proportional to the bromine concentration and can be used to estimate the amount of bromine impurity ions. We estimated this amount by recording the luminescence spectra of our crystals and of crystals known to contain 0.1 mole% Br and excited with the hydrogen lamp radiation of 7.45 eV energy and 10 Å width. An estimate of the bromine impurity concentration gave 0.04 mole%.

The temperature dependence of the luminescence observed in our study is also different from that reported in Ref. 4 for NaCl crystals. The dependence is described satisfactorily by the formula[4]

$$I=\frac{I_0}{1+\nu\tau_0\exp[-E/kT]}, \quad (1)$$

where I_0 is the intensity at T = 0; E is the activation energy; ν is a constant; τ_0 is the spontaneous exciton lifetime.

The continuous curve in Fig. 3 approximates the experimental data for E = 0.13 eV, $\nu\tau_0 = 3.2\cdot10^9$ (5.25 eV band) and for E = 0.22 eV, $\nu\tau_0 = 1.6\cdot10^7$ (3.87 eV band).

Figure 4 shows the luminescence spectrum of a KBr crystal obtained by us at 40°K by excitation with the H_2 laser radiation (λ = 1610 Å). Within the limits of the experimental error, this spectrum agrees with that obtained employing the hydrogen lamp radiation. A 2810 Å (4.42 ± 0.02 eV) band is associated with radiative decay of self-localized σ excitons and agrees with the results reported by others.[5] A wide band at 2.5-3.5 eV is due to unknown impurities. Its intensity depends weakly on temperature. There is no π exciton band at 40°K because at this temperature this band is quenched and also because of the presence of impurities whose luminescence is emitted for 25 μsec at T = 40°K.

Thus, in spite of the much higher power density (approximately ten orders of magnitude higher) achieved with the aid of an H_2 laser, compared with a hydrogen lamp, the basic properties of the luminescence of NaCl and KBr crystals can still be interpreted in a natural manner on the basis of the existing ideas and nonlinear effects are not observed.

4. Intense excitation of alkali-halide crystals should, in principle, produce nonlinear effects in the interaction of excitons with one another; one should also observe amplification and generation of stimulated ultraviolet radiation in alkali-halide crystals.

The possibility of formation of molecular complexes in alkali-halide crystals due to the interaction between excitons was first pointed out in Ref. 7, where the appearance of additional absorption bands of KI and RbI was attributed to the formation of exciton molecules consisting of unrelaxed and self-localized excitons. It was suggested in Ref. 8 that molecular exciton complexes (biexcitons) can appear also in the luminescence spectra because the 5.23 eV band of NaCl, shifted toward longer wavelengths relative to the luminescence band of singlet self-localized excitons, may be attributed to self-localized biexcitons.

We shall now consider the possibility of formation of

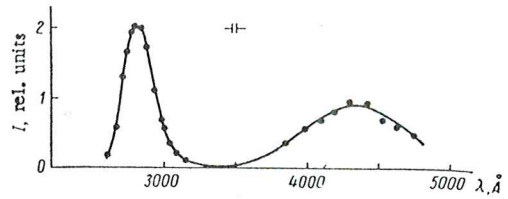


FIG. 4. Luminescence spectrum of a KBr crystal excited with the H_2 laser radiation at T = 40°K.

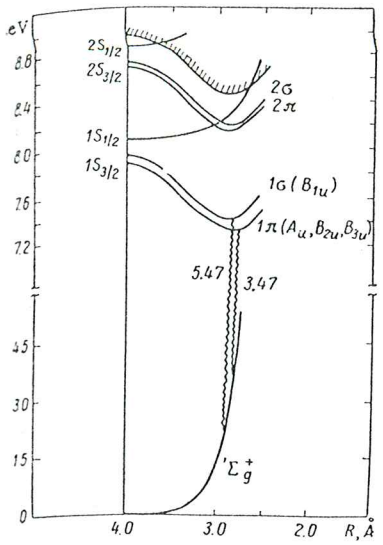
self-localized biexcitons in NaCl at excitation intensities which are attainable with the aid of a hydrogen laser. The most probable process of formation of self-localized biexcitons is that involving collisions between free and self-localized excitons, followed by the relaxation of a free exciton in a molecular complex generated by such a collision. The rate of formation of self-localized biexcitons is

$$\nu_b=\gamma v\sigma N_{ex}, \quad (2)$$

where N_{ex} is the concentration of self-localized excitons; σ is the effective collision cross section; v is the relative velocity of two excitons; γ is the probability of formation of a molecular complex in one collision. Allowing for the effective depth of penetration of the H_2 laser radiation which is $d \approx 10^{-5}$ cm, energy of the laser pulses in our experiments $q \approx 10^{-6}$ J, focusing area S = 0.4 × 0.8 mm = $3\cdot10^{-3}$ cm^2, and reflection coefficient of NaCl which is R = 0.25 in the range under discussion,[9] we find that $N_{ex} = 2\cdot10^{19}$ cm^{-3}. If the collision cross section is estimated using the expression $\sigma = \pi a_0^2$, where a_0 = 2.81 Å is the exciton radius, and v is taken to be the average thermal velocity of free excitons at T = 40°K ($\sigma = 2.5\cdot10^{-15}$ cm^2, $v = 5.2\cdot10^6$ cm/sec), we find that $\nu_b = 2.6\cdot10^{11}\gamma$ sec^{-1}. Thus, in this case the condition for the manifestation of self-localized biexcitons in the luminescence spectra is $\nu_b > \tau^{-1}$, where τ, the lifetime of self-localized excitons, is at the limit of what is possible in our case if biexcitons are formed from singlet excitons ($\tau \approx 5\cdot10^{-9}$ sec) and there is a small margin in the case of participation of triplet self-localized excitons ($\tau = 1.2\cdot10^{-4}$ sec) for $\gamma \sim 10^{-2}$.

The appearance of self-localized biexcitons in alkalide-halide crystals is hindered by the presence of even very small amounts of impurities in the form of heavy halogen atoms and we recall that our experiments indicate that the 5.23 eV band of NaCl should be attributed to the luminescence emitted from relaxing centers formed by bromine.

The conditions for obtaining the stimulated radiation from self-localized excitons in alkali-halide crystals are considered in Refs. 8, 10, and 11. Figure 5 is the luminescence scheme and the structure of levels of self-localized excitons in NaCl calculated on the basis of the model in Ref. 12, used earlier to deal with the luminescence mechanism of crystalline xenon. The singlet and triplet luminescence bands at 5.47 and 3.47 eV, respectively, are due to the radiative annihilation of self-localized excitons of the σ and π types, respectively. After the emission of a photon the system goes over to a lower energy level with a repulsive potential curve. Therefore, the lower level of the transition in question is deactivated during the flight



IG. 5. Structure of the potential curves of self-localized excitons in NaCl nd the luminescence scheme.

part of two atoms ($\sim 10^{-12}$ sec). This deactivation does ot excite local vibrations of a crystal so there is no need in contrast to Ref. 10) to consider the vibrational relaxation of the lower active level. This applies also to the pper level because self-localized excitons usually emit nly from the ground vibrational state.

The optical gain due to the radiative decay of self-ocalized excitons can be expressed in the form

$$g = \tau_l G_0 N_{ex} = \frac{\eta}{4\pi n^2} \sqrt{\frac{\ln 2}{\pi}} \frac{\lambda^2}{\tau \Delta\nu} N_{ex}, \qquad (3)$$

here η is the quantum efficiency of the luminescence band n question; n is the refractive index of the crystal; τ is he spontaneous lifetime; $\Delta\nu$ is the band width; λ is the mission wavelength; N_{ex} is the concentration of self-lo-alized excitons.

In the case of excitation by the H_2 laser radiation in ur study, we have $N_{ex} \sim 2 \cdot 10^{19}$ cm^{-3} (see the estimate btained above), $\tau = 5 \cdot 10^{-9}$ sec, $\lambda = 2310$ Å, $\Delta\nu = 1.4 \cdot 10^{14}$ sec^{-1} so that if $\eta \leq 0.02$, we find that $G_0 = 1.25 \cdot 10^{-17}$ cm^2 and $g \approx 5$ cm^{-1}.

However, this gain is too small to be manifested in our experiments since the effective losses associated with diffraction are $\beta_d \approx 10^2$ cm^{-1}.

Moreover, under optical excitation conditions, when the depth of penetration of the exciting radiation is small, the losses due to the nonradiative surface annihilation of excitations should play an important role and these may reduce the gain by an order of magnitude.

We shall conclude by pointing out that at high rates of excitation, when the exciton concentration reaches such a value that $N_{ex} a_0^3 \sim 0.01$ ($N_{ex} \sim 4 \cdot 10^{20}$ cm^{-3}), in the case of NaCl it should be possible to observe exciton condensation in alkali-halide crystals. This is facilitated by the long lifetime of the triplet self-localized excitons, which is $\sim 10^{-4}$ sec at helium temperatures. In contrast to the electron–hole condensation in Ge and Si, the condensation in alkali-halide crystals may result (because of the self-localization of electrons) in a phase transition accompanied by a change in the crystal lattice. Further experiments will be directed to search for these nonlinear effects in wide-gap crystals subjected to intense VUV excitation.

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